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Authors

Liang, Yan
Zhou, Jini
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et al.

Publication Date

2020-03-01

DOI

10.1016/j.envpol.2019.113803

Peer reviewed



Evidence for the critical role of nanoscale surface roughness on the retention and release of silver nanoparticles in porous media[☆]

Yan Liang^{a, b}, Jini Zhou^a, Yawen Dong^a, Erwin Klumpp^c, Jiří Šimůnek^d,
Scott A. Bradford^{e, *}

^a School of Resources, Environment and Materials, Guangxi University, Nanning, China

^b Guangxi Key Laboratory for Agro-Environment and Agro-Product Safety, Nanning, China

^c Agrosphere Institute, IBG-3, Forschungszentrum Jülich GmbH, Jülich, Germany

^d Department of Environmental Sciences, University of California, Riverside, CA, United States

^e US Salinity Laboratory, USDA, ARS, Riverside, CA, United States

ARTICLE INFO

Article history:

Received 23 August 2019

Received in revised form

9 December 2019

Accepted 10 December 2019

Available online 13 December 2019

Keywords:

Surface roughness

AgNPs

XDLVO

Retention

Release

ABSTRACT

Although nanoscale surface roughness has been theoretically demonstrated to be a crucial factor in the interaction of colloids and surfaces, little experimental research has investigated the influence of roughness on colloid or silver nanoparticle (AgNP) retention and release in porous media. This study experimentally examined AgNP retention and release using two sands with very different surface roughness properties over a range of solution pH and/or ionic strength (IS). AgNP transport was greatly enhanced on the relatively smooth sand in comparison to the rougher sand, at higher pH, and lower IS and fitted model parameters showed systematic changes with these physicochemical factors. Complete release of the retained AgNPs was observed from the relatively smooth sand when the solution IS was decreased from 40 mM NaCl to deionized (DI) water and then the solution pH was increased from 6.5 to 10. Conversely, less than 40% of the retained AgNPs was released in similar processes from the rougher sand. These observations were explained by differences in the surface roughness of the two sands which altered the energy barrier height and the depth of the primary minimum with solution chemistry. Limited numbers of AgNPs apparently interacted in reversible, shallow primary minima on the smoother sand, which is consistent with the predicted influence of a small roughness fraction (e.g., pillar) on interaction energies. Conversely, larger numbers of AgNPs interacted in deeper primary minima on the rougher sand, which is consistent with the predicted influence at concave locations. These findings highlight the importance of surface roughness and indicate that variations in sand surface roughness can greatly change the sensitivity of nanoparticle transport to physicochemical factors such as IS and pH due to the alteration of interaction energy and thus can strongly influence nanoparticle mobility in the environment.

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1. Introduction

The transport and retention of colloids (e.g., microorganisms, clays, organic matter, and nanoparticles) in porous media strongly influences their fate in the environment (Bradford et al., 2002; Wang et al., 2016; Fazeli Sangani et al., 2018; Molnar et al., 2019). Colloid filtration theory considers that retention in porous media is dependent on the mass transfer rate from the bulk solution to the

collector surface, and the sticking efficiency on the collector (grain) surface (Yao et al., 1971). Several correlation equations have been developed to predict the colloid mass transfer rate to collector surfaces as a function of the water velocity, the size of the colloid and the collector, and the colloid density (Tufenkji and Elimelech, 2004; Messina et al., 2015). The sticking efficiency has commonly been related to the solution chemistry (e.g., pH, ionic strength, cation type), flow velocity (Torkzaban et al., 2007; Shen et al., 2010), and the size and surface properties (charge, surface coating) of the collector and colloid (Lin et al., 2011; Flory et al., 2013; Park et al., 2016).

The sticking efficiency of colloids on collector surfaces is normally related to interaction energy calculations which are used to

[☆] This paper has been recommended for acceptance by Baoshan Xing.

* Corresponding author.

E-mail address: scott.bradford@ars.usda.gov (S.A. Bradford).

determine the favorability and strength of colloid adhesion. The interaction energy is frequently assumed to depend on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). Interaction energy calculations normally assume that the colloid and collector surfaces are chemically homogeneous and smooth. In contrast, the surface of natural porous media exhibits pronounced roughness, which can be as high as several hundreds of nanometers or micrometers for a sand surface (Shellenberger and Logan, 2002; Shen et al., 2011; Konopinski et al., 2012; Jin et al., 2015; Rasmuson et al., 2017; Johnson et al., 2018; Rasmuson et al., 2019; Ron et al., 2019). It has been widely acknowledged that surface roughness is one of the important factors causing deviations between experimental and theoretical results (Rabinovich et al., 2000; Katainen et al., 2006). The roughness properties of a collector and colloid are important for predicting colloid retention (Jin et al., 2015; Ron et al., 2019). Surface roughness can dramatically alter the colloid retention and release by altering the interaction energy profiles. For example, the repulsive energy barrier and depths of the primary and secondary minima are lowered or eliminated on top of nanoscale convex asperities, and the energy barrier can be eliminated and the depth of the primary minimum can be increased at the bottom of nanoscale convex asperities (Suresh and Walz, 1996; Bhattacharjee et al., 1998; Hoek et al., 2003; Hoek and Agarwal, 2006; Bradford and Torkzaban, 2013; Shen et al., 2019). In addition, surface roughness will modify the flow field adjacent to the solid surface, increase the lever arm for the resisting adhesive torque, and decrease and/or eliminate the lever arm for the applied hydrodynamic torque (Burdick et al., 2005; Bradford et al., 2013). These roughness effects can enhance colloid retention on electrostatically repulsive surfaces and diminish retention on electrostatically attractive surfaces (Bradford et al., 2017). Weaker adhesive interactions on rough surfaces contribute to colloid removal by diffusion and/or hydrodynamics (Bradford and Torkzaban, 2015) and can explain colloid release from primary minima under increasingly unfavorable conditions (Shen et al., 2018). Coupled effects of hydrodynamic slip and colloid-surface interactions with asperities can decrease the gap between favorable and unfavorable conditions and influence colloid detachment during ionic strength (IS) and flow perturbations (Rasmuson et al., 2019; Ron et al., 2019). Bradford et al. (2017) demonstrated that roughness conditions that contribute to colloid retention change with the solution chemistry and charge of surfaces. Although theoretical calculations have demonstrated that surface roughness has a large influence on colloid retention and release, relatively little experimental research has examined these issues, especially under different solution chemistry conditions (Shen et al., 2011; Shen et al., 2012; Torkzaban and Bradford, 2016; Rasmuson et al., 2019). Furthermore, this experimental research has not been compared with theoretical calculations that account for nanoscale roughness.

Silver nanoparticles (AgNPs) are one of the most widely used nanomaterials (Nowack et al., 2011; Vance et al., 2015). There is concern about the inevitable release of AgNPs into the environment (Yu et al., 2013; McGillicuddy et al., 2017) and the potential adverse effect on human health and the environment (León-Silva et al., 2016; Rezvani et al., 2019). Various physicochemical factors have been demonstrated to strongly influence the transport of AgNPs, e.g., grain size of the collector, the solution IS and pH, and the presence of stabilizers (Lin et al., 2011; Flory et al., 2013; Liang et al., 2013b; Park et al., 2016; Adrian et al., 2018; Neukum, 2018). However, previous transport studies may provide incorrect or incomplete interpretations because they have largely neglected the role of nanoscale surface roughness on AgNP retention and release. In this work, AgNP transport experiments were therefore conducted

in mixtures of two sands with the same size range and surface chemical properties, but very different surface roughness conditions. The retention behavior of AgNPs on these sands was studied under various solution IS and pH. Interaction energy calculations that accounted for various sand roughness properties and numerical simulations were performed to deduce the governing mechanisms of retention and release. The findings from this study improve our understanding and description of colloid interactions and transport behavior in the environment.

2. Materials and methods

2.1. Solution chemistry

Ultrapure water and KNO_3 were used to make electrolyte solutions with an IS of 5, 10, 20, 40, and 50 mM. The unadjusted pH of these solutions was around 6.5. NaOH and HNO_3 were employed to adjust the pH values in some 5 mM KNO_3 solutions to 4, 8, 8.5, 9.0, and 10.

2.2. Quartz sand

Two analytically pure quartz sands were employed in column experiments. One was purchased from Quarzwerke GmbH, Germany (denoted as QW sand) and was prepared by cleaning and sieving of natural raw materials, whereas the other was obtained from Tianjin Guangfu Fine Chemical Research Institute, China (denoted as GF sand) and was produced by comminution of quartzite. To minimize the influence of chemical heterogeneities on the sand surfaces, purification procedures for sands were performed, including boiling in HNO_3 and H_2O_2 in a high borosilicate glass reactor with constant stirring, rinsing with deionized water, and drying to minimize the trace amount of metal oxides and organic impurities (Liang et al., 2013b). Characterization of the sands for physicochemical properties including surface morphology (images and roughness parameters), grain size distribution parameters, specific surface area, streaming potential, and chemical composition (Al, Fe, Mg, and Ca) on the surface was described in section S1 of the supporting information (SI).

2.3. AgNPs

Raw AgNP suspension (10.16% w/w) was purchased from AgPURE™, rent a scientist® GmbH, Germany. This product was OECD reference NM-Series of representative manufactured nanomaterials (NM-300 silver). The manufacturer reported that the AgNPs were stabilized using a mixture of two non-ionic surfactants, 4% w/w each of Polyoxyethylene Glycerol Trioleate and Polyoxyethylene (20) Sorbitan mono-Laurat (Tween 20). The stability, homogeneity, and solubility of this material were characterized and described in detail in previous research (Kaegi et al., 2011; Klein et al., 2011; Liang et al., 2013b). In general, the AgNPs were spherical and the size measured by the transmission electron microscope (TEM) was 15–20 nm (Liang et al., 2013b). AgNP suspension for each experiment was freshly prepared by diluting the raw concentrated suspension into KNO_3 solutions and then sonicated for 15 min in a sonication bath. The initial AgNP suspension concentration was determined to be approximately 10 mg L^{-1} using an inductively coupled plasma-mass spectrometry (ICP-MS) after dissolving with 30% HNO_3 . The zeta potentials and the hydrodynamic diameters of AgNPs in selected solution chemistries were measured with a ZetaSizer Nano ZS90 (Malvern Instruments, Worcestershire, U.K.) and then used in interaction energy calculations.

Concentrations of AgNPs in transport studies were determined

using a UV–Vis spectrophotometer (Thermo Scientific, TM Evolution 300, U.S.) with a fixed scan at a wavelength of 413 nm (R^2 of calibration curves ≥ 0.9995 and the detection limit was 0.05 mg L^{-1}). The AgNP suspension was determined to be stable by comparison of UV–vis absorbance readings of input AgNP suspensions for the considered solution chemistries (pH from 4 to 10 and IS from 5 to 50 mM KNO_3) over the duration of experiments. The dissolution of AgNPs was also found to be negligible (less than 1% of the total mass) for similar conditions (Kaegi et al., 2011; Klein et al., 2011; Liang et al., 2013b).

2.4. Transport experiments

Water saturated column experiments were performed following the protocols outlined in Liang et al. (2013b). In brief, quartz sand was wet-packed in a stainless-steel column with a 3 cm inner diameter and 12 cm length. A peristaltic pump was used to inject solution and AgNP suspension into the columns in an upflow mode. The input concentration of AgNPs was fixed at 10 mg L^{-1} and the Darcy velocity was kept constant at around 0.7 cm min^{-1} in all column experiments. Transport experiments were conducted in the following steps: (1) the packed column was conditioned with around 50 pore volumes (PVs) of KNO_3 background solution; (2) 100 mL tracer (KNO_3 solution at 2 to 5-fold concentration of the background solution) was introduced into the column followed by irrigation of at least 5 PVs background solution; (3) 100 mL AgNP suspension was then injected into the column and rinsed by around 3 PVs of the same KNO_3 solution until the normalized concentration was less than 1%. Breakthrough curves (BTCs) of tracer were determined from conductivity measurement on collected effluent samples, whereas BTCs of AgNPs were obtained by determining the concentrations of effluent samples using a UV–Vis spectrophotometer.

Mixtures of QW and GF sands - Two types of sand with different surface structures and properties at mass ratios of QW:GF = 0:1, 1:2, 1:1, 2:1, and 1:0 were homogeneously mixed before they were packed into the columns for transport experiments. The IS was 5 mM KNO_3 and the other experimental procedures were the same as described above.

Transport of AgNPs under different IS - Column experiments were carried out to investigate the retention of AgNPs on a relatively smooth GF sand surface under different IS (5, 10, 20, 40, and 50 mM KNO_3) conditions.

Different pH values of the column system - pH values of 4.0, 6.5 (unadjusted), 8.0, 8.5, 9.0, and 10 were selected for each column experiment using rough QW sand at IS of 5 mM, while pH values of 6.5 (unadjusted) and 8.0 were selected for experiments with GF sand at IS = 50 mM. The pH in KNO_3 , tracer, and AgNP suspension were all adjusted to a selected value in a given column experiment.

2.5. Release experiments

AgNPs were initially retained in the presence of 5 mM KNO_3 on rough QW sand and 40 mM KNO_3 on relatively smooth GF sand in a similar manner to section 2.4 and then subject to a 20-h flow interruption (phase I). The release of AgNPs was then initiated by flushing the column with several PVs of ultrapure water: (i) with an unadjusted pH (pH 6.5) (phase II); (ii) at pH = 10 (phase III); and (iii) at pH = 10 after a 20 h flow interruption (phase IV). Finally, the sand was excavated from the column and placed into a container containing excess amounts of ultrapure water at pH 10 (phase V). The container was slowly shaken for several minutes to investigate the release of the remaining retained AgNPs by determination of the AgNP concentration, the volume of water, and the mass of dry sand.

2.6. Theory and model

Interaction energy calculations that considered various surface roughness properties and numerical simulations were performed to better understand mechanisms contributing to AgNP retention and release under the tested solution chemistries. The interaction energy calculations based on conventional DLVO theory (smooth surface) was applied with and without consideration of steric interactions. The approach of Bradford et al. (2017) was employed to determine the interaction energy (Φ , MLT^{-1}) between AgNP and sand with nanoscale roughness as a linear combination of interaction energies for various nanoscale roughness components. Section S2 of the SI provides details pertaining to these calculations for AgNP-sand interactions. The dimensionless depths of the primary ($\Phi_{1\text{min}}$) and secondary ($\Phi_{2\text{min}}$) minima, the energy barrier height (Φ_{max}) and the energy barrier to detachment from the primary minimum ($\Delta\Phi_d = \Phi_{\text{max}} - \Phi_{1\text{min}}$) were obtained by analyzing the interaction energy profiles.

Section S3 in the SI describes the modeling approach in detail. The retention rate coefficient (k_1) and the normalized maximum solid phase concentration of deposited AgNPs (S_{max}/C_0 , where C_0 is the AgNP input concentration) for blocking were optimized. The fitted values of S_{max} were then used to calculate the fraction of the grain surface area that contributes to AgNP retention (S_f).

3. Results and discussion

3.1. Characterization of AgNPs and quartz sands

Table S1 lists measured zeta potentials of AgNPs and quartz sands, and hydrodynamic diameters (d_p) of AgNPs over the range of solution chemistries that were used in column experiments. The zeta potential of AgNPs gradually increased from -22.6 ± 1.6 to -7.4 ± 1.0 mV when the IS increased from 5 to 50 mM KNO_3 at pH = 6.5 and became more negative as the pH increased from 4.0 to 10.0 at 5 mM KNO_3 . The AgNP d_p values slightly increased as the IS increased from 5 to 50 mM KNO_3 at pH = 6.5 and decreased as the pH increased from 4.0 to 10.0 at 5 mM KNO_3 . These relatively minor changes in d_p over a large range in pH and IS reflect the stability of the AgNP suspensions in the presence of adsorbed surfactants (Adrian et al., 2018), which is normally attributed to steric interactions (Hotze et al., 2010). Note that the size determined by the Zeta-sizer is normally larger than by TEM because measurement by the Zeta-sizer is biased toward a larger size fraction and takes a value of hydrodynamic diameter that can also be influenced by the thickness of the surfactant coating (Diegoli et al., 2008; Klein et al., 2011). The zeta potential of the QW sand decreased from -29.0 ± 0.8 to -57.3 ± 3.8 mV when the solution pH increased from 4.0 to 10.0 under 5 mM KNO_3 due to deprotonations of the surface. The zeta potentials of GF sand became less negative when the IS was increased from 5 to 50 mM KNO_3 under pH 6.5 due to compression of the double layer thickness and charge screening.

The mean grain sizes (d_{50}) of mixtures with different proportions of rough and relatively smooth sand (mass ratios of 0:1, 1:2, 1:1, 2:1, and 1:0) ranged between 503 and 519 μm , indicating that the two sands were almost at the same size. Microscope images (Figs. S1 and 1) show the significant difference of the surface topography of the two sands. Table S2 presents surface morphological parameters, chemical analysis, and BET surface areas for both purified sands. The average roughness was 418 ± 150 and 78 ± 41 nm for the relatively rough QW and smoother GF sand, respectively, while the surface chemistry and surface area of both sands were generally comparable. Surface roughness is therefore the main difference between the surface properties of these two sands.

3.2. Interaction energy calculations

Measured values of d_p and zeta potential were used to calculate the conventional interaction energy profiles for different IS with (Fig. S2a) and without steric interactions (Fig. S2b). The magnitude of Φ_{2min} (<0.33) was always much less than the average kinetic energy fluctuations for diffusing colloids (e.g, 1.5) (Bradford and Torkzaban, 2015) and was therefore not considered to contribute to AgNP retention. Parameter values of Φ_{1min} , Φ_{max} , and $\Delta\Phi_d = \Phi_{max}-\Phi_{1min}$ for the AgNP-sand interactions without consideration of steric interaction are given in Table S1. Table S1 shows a general trend of decreasing Φ_{max} with decreasing pH and increasing IS because of less negative values of the zeta potentials and compression of the double layer thickness at higher IS. However, AgNPs can only diffuse over Φ_{max} into Φ_{1min} when $\Phi_{max} < 6$ to 10 (Bradford and Torkzaban, 2015). Primary minimum interactions are therefore predicted in GF sand when $IS \geq 40$ mM and in QW sand when $pH = 4$. No retention is predicted for other solution chemistry conditions. Additionally, if steric interactions from the adsorbed surfactant layer on the AgNPs are included in the interaction energy calculations then a very large energy barrier occurs (Fig. S2b) and no AgNP retention is predicted for all considered solution chemistry conditions. These findings reveal the deviations between experimental results and theoretical calculations based on the conventional interaction energy calculations even if the steric interactions are included.

3.3. AgNP retention in the sand with a rough surface

Column experiments were carried out to investigate the influence of sand roughness on AgNP transport and retention by creating quartz sand with different mass ratios of relatively rough QW and smoother GF sands. Fig. 2 shows observed and simulated AgNP BTCs for mixtures of QW and GF sand with mass ratios of 0:1, 1:2, 1:1, 2:1, and 1:0 when the $IS = 5$ mM KNO_3 and $pH = 6.5$ (unbuffered). BTCs were plotted as normalized effluent concentrations (C/C_0) versus pore volumes. Table 1 summarizes the

experimental conditions, the mass recoveries from BTCs, and the fitted model parameters.

Fig. 2 clearly demonstrates that AgNP retention is significantly different for various mass ratios of these two sands. The mass recovery of AgNPs in the effluent (M_{eff}) and the fitted parameters of k_1 and S_{max}/C_0 present an approximately linear correlation with the mass percentage of the relatively rough QW sand to the total amount of quartz sand (M_{QW}) (Fig. S3 A1, B1, and C1). Larger M_{QW} resulted in stronger AgNP retention and larger values of k_1 and S_{max}/C_0 (Table 1). Fig. 2 also shows systematic blocking trends (the gradual ascent trend of the BTCs due to a decrease in AgNP retention over time as retention sites are blocked or filled) which exhibit a delay in AgNP breakthrough and then increasing concentrations of AgNPs in the effluent. These blocking effects can be explained by the rate of filling of a limited number of retention sites. In particular, blocking/filling of retention sites is expected to occur more rapidly for larger k_1 and smaller S_{max} (Leij et al., 2015). The value of S_f (Eq. [S11]) shown in Table 1 was less than 5.3% and 0.8% for geometric and BET surface area estimates, respectively. Consequently, only a very small fraction of the QW sand surface area contributed to AgNP retention. SEM images taken from the samples for both QW and GF sand after completion of transport experiments show large AgNP-free areas (Fig. S4) and this information is consistent with the calculated values of S_f .

AgNP retention in Fig. 2 is not consistent with interaction energy calculations for smooth and chemical homogeneous surfaces (Fig. S2 and Table S1). In particular, no AgNP retention on the relatively rough QW and GF sands is predicted when the $pH = 6.5$ and the $IS = 5$ mM KNO_3 because $\Phi_{max} > 10$. Furthermore, differences in AgNP retention on QW and GF sands are not predicted because values of Φ_{max} were nearly identical (39.4 and 40.1 for QW and GF sand, respectively). Potential explanations for these discrepancies include nanoscale charge heterogeneity and roughness which can locally reduce and/or eliminate the energy barrier (Suresh and Walz, 1996; Bhattacharjee et al., 1998; Hoek et al., 2003; Hoek and Agarwal, 2006; Bradford and Torkzaban, 2013; Bradford et al., 2017; Bradford et al., 2018). Nanoscale chemical

Table 1
Experimental Parameters and Fitted/Calculated Values (k_1 , S_{max}/C_0 , and S_f) of AgNP Transport under Various Experimental Conditions.

	Exp. Name	M_{QW}	IS mM	pH	M_{eff} , %	k_1 , min ⁻¹	S_{max}/C_0 , cm ³ g ⁻¹	S_f % BET	S_f % Geometric	R^2
Fig. 2	QW:GF = 0:1	0.00	5	6.5	79.2	0.346	0.166	0.236	0.645	0.997
	QW:GF = 1:2	0.33	5	6.5	45.3	0.409	0.443	0.445	1.787	0.966
	QW:GF = 1:1	0.50	5	6.5	21.2	0.485	0.713	0.584	2.722	0.949
	QW:GF = 2:1	0.67	5	6.5	8.5	0.741	0.964	0.669	3.549	0.979
	QW:GF = 1:0	1.00	5	6.5	1.5	1.026	1.467	0.800	5.279	0.951
Fig. 3	pH = 4.0	1.00	5	4.0	0.2	1.378	2.199	1.272	8.393	0.443
	pH = 6.5	1.00	5	6.5	1.5	1.026	1.467	0.800	5.279	0.951
	pH = 8.0	1.00	5	8.0	17.8	0.383	1.195	0.693	4.571	0.981
	pH = 8.5	1.00	5	8.5	51.2	0.234	0.424	0.252	1.659	0.984
	pH = 9.0	1.00	5	9.0	71.8	0.148	0.233	0.145	0.955	0.977
	pH = 10.0	1.00	5	10.0	86.3	0.049	0.114	0.069	0.453	0.981
	5 mM	0.00	5	6.5	79.2	0.346	0.166	0.236	0.645	0.997
Fig. 4	10 mM	0.00	10	6.5	49.6	0.751	0.436	0.880	2.401	0.970
	20 mM	0.00	20	6.5	39.7	1.091	0.537	0.846	2.310	0.969
	40 mM	0.00	40	6.5	8.8	1.313	0.767	1.164	3.177	0.965
	50 mM	0.00	50	6.5	0.0	1.622	1.947	2.953	8.060	0.406
Fig. S5	pH 6.5	0.00	50	6.5	0.0	1.622	1.947	2.953	8.060	0.406
	pH 8.0	0.00	50	8.0	78.1	0.632	0.183	0.378	1.031	0.967
Fig. 5					M_{eff}	M_I	M_{II}	M_{III}	M_{IV}	M_V
	GF sand	0	5	6.5	8.8	0.1	18.2	70.6	5.0	<0.1
	QW sand	1.00	40	6.5	1.3	0.1	2.1	14.7	12.8	5.2

QW and GF denote rough and relatively smooth sand, respectively; M_{QW} , mass percentage of rough QW sand in columns; M_{eff} , the mass percentages of AgNPs recovered from effluent; $M_I - M_V$, the mass percentages of AgNPs recovered from phase I – V in release experiments; k_1 , the first-order retention coefficient; S_{max}/C_0 , normalized maximum solid phase concentration of deposited NPs; S_f , the fraction of the grain surface area that contributes to AgNP retention, BET and geometric denote S_f calculation based on BET measurements and geometric estimates, respectively; R^2 , Pearson's correlation coefficient. Constant Darcy velocity = 0.7 cm min⁻¹ and $C_0 = 10$ mg L⁻¹ were employed in all experiments.

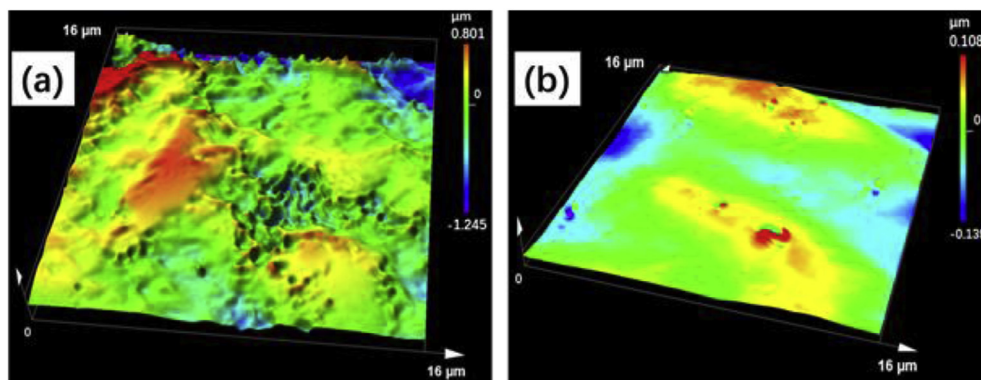


Fig. 1. Laser scanning confocal microscope images of rough sand (a) and relatively smooth sand (b) used for column experiments.

heterogeneity that is larger than a critical size can create regions on a net unfavorable surface that are favorable for interaction between the colloid and the solid surface due to a local reduction in the energy barrier and an increase in the depth of the primary minimum. However, differences in nanoscale chemical heterogeneity are not expected to be the primary cause for the observed AgNP retention behavior on QW and GF sands because: (i) both sands were chemically treated to minimize chemical heterogeneity; (ii) concentrations of major cations in the acid digest of the sands were similar (Table S2); (iii) the predicted energy barrier was nearly identical when using measurements of sand streaming potential (Table S1); and (iv) previous studies have demonstrated that interaction energy profile properties are more sensitive to nanoscale roughness than charge heterogeneity (Bradford et al., 2017).

Significant differences in the roughness properties of QW and GF sands (Fig. 1, Fig. S1, and Table S2) provide a plausible alternative explanation for differences in AgNP retention in Fig. 2. The energy barrier to the primary minimum at $IS = 5$ mM and $pH = 6.5$ was high enough to inhibit most AgNP retention on the relatively smooth GF sand (Table S1). Conversely, the roughness properties of the QW sand greatly enhanced AgNP retention. Interaction energy calculations have demonstrated that the tops of nanoscale roughness pillars can locally reduce and/or eliminate the energy barrier and the depth of the primary minimum (Shen et al., 2012; Bradford

et al., 2017). These roughness effects on interaction energies are magnified for locations with smaller roughness fractions (e.g., pillar diameters) and when roughness occurs on both the colloid and sand surface (Bradford et al., 2017). Diffusive or hydrodynamic removal of colloids from a primary minimum may occur in some cases depending on the local roughness properties (Torkzaban and Bradford, 2016; Bradford et al., 2017). Concave locations between protruding roughness asperities also influence the interaction energy profiles (Shen et al., 2012; Li et al., 2017). The energy barrier can be reduced or eliminated at the vertices of these locations because repulsive forces on AgNPs act in opposite directions and cancel out (Li et al., 2017). Colloids that are retained in concave locations are less susceptible to removal by hydrodynamic forces and/or IS reduction than on pillar tops (Li et al., 2017). These observations indicate that the greater k_d , larger S_{max}/C_0 , and stronger retardation in the QW sand (Fig. S3) were mainly produced by sand surface roughness properties.

3.4. Sensitivity of AgNP retention to pH in rough QW sand

Transport experiments were carried out to better understand the pH dependence of AgNP retention on relatively rough QW sand. Fig. 3 presents observed and simulated BTCs for AgNPs in the relatively rough QW sand when the solution $IS = 5$ mM KNO_3 and

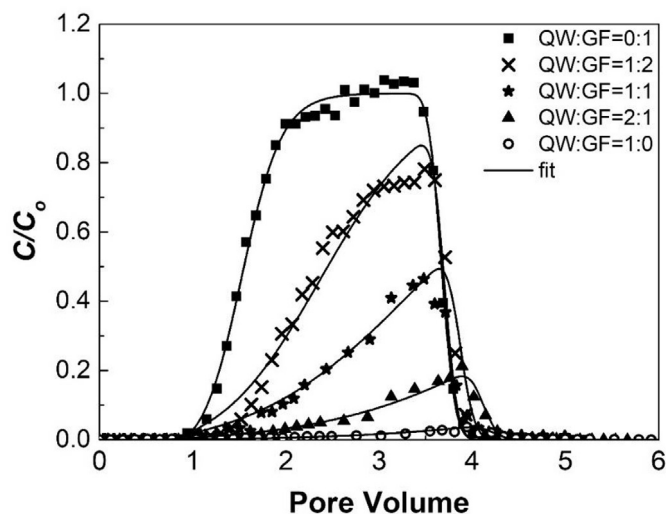


Fig. 2. Observed and fitted breakthrough curves of AgNPs in various mixture ratios of rough and relatively smooth sand (QW and GF denote rough and relatively smooth sand, respectively) when the $IS = 5$ mM KNO_3 and $pH = 6.5$. Lines were fitted results.

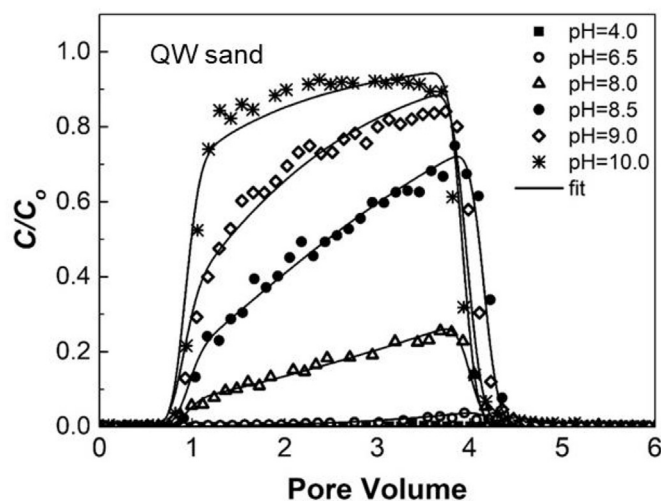


Fig. 3. Observed and fitted breakthrough curves of AgNPs under various pH values in rough sand (QW denotes rough sand) when the $IS = 5$ mM KNO_3 . Lines were fitted results.

the pH = 4.0, 6.5, 8.0, 8.5, 9.0, and 10.0. Results show that an increase in pH resulted in gradual enhancement of AgNP transport. Fitted values of k_1 and S_{\max}/C_0 when the solution pH = 4.0 were nearly 30-fold higher than those obtained when the pH = 10.0 (Table 1). Moreover, the fitted k_1 and S_{\max}/C_0 were inversely proportional to the pH values (Fig. S3 B2 and C2). Additionally, the retardation of the AgNP breakthrough was gradually diminished when the solution pH was increased.

AgNP attachment is inhibited or eliminated when Φ_{\max} is greater than around 5.7 (Bradford and Torkzaban, 2015). The value of Φ_{\max} tends to increase with pH because of more negative zeta potentials and greater electrostatic repulsion (Table S1). This increase in Φ_{\max} with pH will therefore decrease the roughness effects that contribute to AgNP retention. Table S3 gives an example of the influence of roughness on Φ_{\max} when pH = 4 and 10 and the IS = 5 mM. Table 1 also indicates that the fraction of the geometric surface area that contributed to AgNP retention (S_f) dramatically decreased from 8.39% to 0.45% as the pH was increased from 4 to 10, respectively. BET estimates of S_f were even smaller.

3.5. AgNP retention in the sand with a relatively smooth surface

Fig. 4 shows observed and simulated AgNP BTCs in the relatively smooth GF sand when the solution IS equaled 5, 10, 20, 40, 50 mM KNO₃ at pH 6.5. Experimental results indicate that the AgNP retention and retardation of the BTCs were significantly increased with the IS. No breakthrough was observed when the IS was 50 mM KNO₃. A number of column studies have previously observed the trend of increasing AgNP retention (Lin et al., 2011; Liang et al., 2013a; Liang et al., 2013b; Braun et al., 2015) and retardation with IS (Liang et al., 2013a; Adrian et al., 2018). Generally, the optimized simulations provided a good description of the BTCs when AgNPs broke through ($R^2 > 0.96$). Fitted values of k_1 and S_{\max}/C_0 systematically increased with IS, whereas calculated M_{eff} decreased with IS (Table 1). Similar blocking behavior was observed and discussed in section 3.3.

Trends for AgNP BTCs, and fitted and calculated parameters with IS can be partially explained by the decrease in energy barrier with IS when the double layer was compressed (Fig. S2a). However, these interaction energy calculations predict that the entire surface area of the GF sand will equally contribute to AgNP retention and all

particles will be retained when the IS = 40 and 50 mM. In contrast, Fig. 4 and Table 1 show a systematic difference in the AgNP transport behavior and fitted and calculated parameters with increasing IS. In particular, k_1 and S_{\max}/C_0 increase with IS. In addition, calculated values of S_f in Table 1 indicate that only a small fraction of the GF sand surface area contributed to AgNP retention, even for the favorable condition when the IS = 50 mM (S_f is less than 8.06% and 2.95% for geometric and BET estimates of surface area, respectively).

Significant amounts of nanoscale surface roughness occur even on the relatively smooth GF sand (Table S2). Particularly, the gradual variation of AgNP retention with increasing IS (Fig. 4) further demonstrates the important role of surface roughness, which results in differences in the energy barrier high and the depth of the primary minimum depending on IS. Otherwise, the AgNP retention would vary sharply with increasing IS due to the transition from unfavorable (no retention) to favorable (complete retention) interactions. Research has also demonstrated that the nanoscale roughness fraction has a larger influence on the shape of the interaction energy profile than the roughness height and that a small roughness fraction and height can produce shallow primary minimum on pillar tops that are susceptible to diffusive or hydrodynamic release (Bradford et al., 2017). This can produce portions of the surface area that are unfavorable for AgNP, even when favorable conditions are predicted on smooth surfaces (Zhang et al., 2016; Bradford et al., 2017). Furthermore, the roughness parameters that contribute to irreversible colloid retention have been observed to change and increase with the solution IS (Bradford et al., 2017). Consequently, roughness may also help to explain the trends of AgNP retention with IS (e.g., increasing k_1 and S_{\max}/C_0 with IS), even on the relatively smooth GF sand (Bradford et al., 2017).

Fig. S5 presents observed and simulated AgNP BTCs in the relatively smooth GF sand when the solution IS = 50 mM KNO₃ and the pH = 6.5 and 8.0. The AgNP transport was greatly enhanced when the solution pH was increased from 6.5 (no breakthrough) to 8.0 (78.1% recovered in the effluent). Note that this enhancement in AgNP transport with increasing pH on the relatively smooth GF sand at IS = 50 mM (Fig. S5) was much greater than for the rough QW sand at IS = 5 mM (Fig. 3). This implies that changes in the interaction energy profile when the pH changed from 6.5 to 8.0 had a larger influence on AgNP retention with the relatively smooth GF sand at IS = 50 mM than on the rougher QW sand at IS = 5 mM. The probability of AgNPs to diffuse into the primary minimum rapidly increases from 0 to 1 as the energy barrier decreases from around 5.7 to 0 (Bradford and Torkzaban, 2015). Consequently, this increased sensitivity to pH likely reflects differences in the energy barrier heights. In particular, AgNP attachment occurs more readily for the lower energy barrier on the GF sand at IS = 50 mM than for the higher energy barrier on the QW sand at IS = 5 mM (Table S1).

3.6. Release of retained AgNPs from quartz sands with different roughness

Additional experiments were conducted to study the release behavior of AgNPs from QW and GF sands. To achieve similar amounts of AgNP retention, the initial deposition occurred at an IS = 5 mM KNO₃ and pH = 6.5 in the relatively rough QW sand, and for the relatively smooth GF sand an IS = 40 mM KNO₃ and pH = 6.5 was employed. Fig. 5 presents the release behavior of retained AgNPs under various solution and flow interruption conditions that are summarized in the figure caption. Release phase I consisted of a 20 h flow interruption followed by continued elution with the same particle-free electrolyte solution as during the deposition phase. There was only a negligible amount (0.1%) of AgNPs detected in the effluent for both sands (Table 1). This implies that the retained

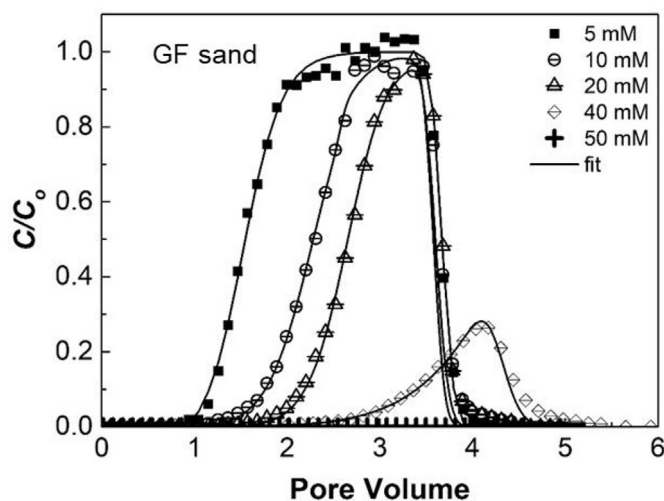


Fig. 4. Observed and fitted breakthrough curves of AgNPs under various ionic strength in relatively smooth sand (GF denotes relatively smooth sand) when the pH = 6.5. Lines were fitted results.

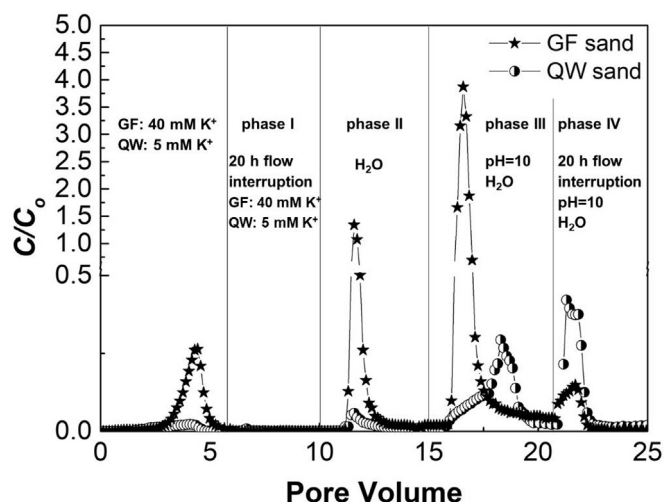


Fig. 5. AgNP release from relatively smooth and rough sand (QW and GF denote rough and relatively smooth sand, respectively). AgNP retention occurred at 40 and 5 mM KNO₃, respectively; release of AgNPs was initiated by 20 h interruption flow with 40 and 5 mM KNO₃ (phase I, pH = 6.5), eluting with ultrapure water (phase II, pH = 6.5; phase III, pH = 10) and 20 h interruption flow with ultrapure water (phase IV, pH = 10).

AgNPs were interacting on the collector surface in a primary minimum that was strong enough to overcome the strength of diffusion; e.g., the energy barrier to detachment was larger than 5.7.

The eluting solution IS was reduced from 5 to 40 mM KNO₃ for the QW and GF sands, respectively, to that of ultrapure water at pH = 6.5 during release phase II (Fig. 5). Only a small fraction of the retained AgNPs was released from the relatively rough QW sand (2.1%), whereas a much larger fraction was released from the relatively smooth GF sand (18.2%). Furthermore, the AgNP release pulse occurred very rapidly from the smoother GF sand and then exhibited lower amounts of release. Note that release with a reduction in IS cannot be explained by the elimination of the secondary minimum because it was not deep enough for colloid immobilization in 5 or 40 mM KNO₃ solution. Furthermore, colloid release with IS reduction from a deep primary minimum from charge heterogeneity on a smooth grain surface is not possible due to an increase in the energy barrier (Shen et al., 2018). Conversely, colloid release with IS reduction may occur from shallow primary minima that happen on tops of nanoscale roughness asperities like pillars (Shen et al., 2018) or fractal surfaces (Shen et al., 2018; Wang et al., 2019), but not from concave locations between roughness asperities because attachment (in primary minima) is irreversible to IS reduction in these valley areas (Li et al., 2017; Wang et al., 2019). The difference in the AgNP release with IS reduction apparently reflects retention on asperities with a shallower primary minimum on the smoother GF sand than the rougher QW sand, e.g., GF sand may contain a smaller roughness fraction or more nanoscale asperities (Wang et al., 2019) than the rougher QW sand.

The pH was increased from 6.5 to 10 while maintaining very low IS conditions (ultrapure water) during phase III of the release experiment (Fig. 5). An additional 14.7% and 70.6% of the retained AgNPs were released from the rougher QW and smoother GF sands, respectively (Table 1). Similar to phase II, AgNP release from the smoother GF sand was again very rapid, and then exhibited lower amounts of release. Conversely, the release of AgNPs from the rougher QW sand was slower than the smoother GF sand, and it gradually reached a peak concentration value at a later time due to slow diffusive release from deeper primary minima. These trends

are generally consistent with those observed during phase II, which were attributed to shallower primary minima on the smoother GF sand due to a smaller roughness fraction. The additional AgNP release when the pH was increased from about 6.5 during phase II to 10 during phase III can be explained by a further decrease and/or elimination of the energy barrier to detachment for certain roughness conditions (Torkzaban and Bradford, 2016) when the zeta potential magnitudes were increased (Table S1). Phase IV of the release experiment (Fig. 5) employed a 20 h flow interruption and was followed by continued elution of ultrapure water at pH = 10. About 12.8% and 5.0% of the retained AgNPs were released from the rougher QW and smoother GF sands, respectively. Similar release kinetics were observed during phases I through IV. However, a higher release pulse was obtained for the rougher QW than the smoother sand. This occurs because all injected AgNPs were recovered after phase IV from the smoother GF sand (Table 1), while the 20 h flow interruption (after eluting with water at pH 10) allowed for increased time for diffusive release from the shallow primary minima or from low flow regions such as concave locations on the rougher QW sand.

Only 5.2% of retained AgNPs was recovered when the rougher QW sand was excavated from the column and placed in a container with ultrapure water at pH 10 and gently shaken for a few minutes (phase V). Furthermore, less than 40% of the retained AgNPs were collected during release phases I-V for the rougher QW sand. The low total recovery of the AgNPs from the QW sand indicates that remaining AgNPs were retained in a deep primary minimum that was stronger than forces from random kinetic energy fluctuations and/or hydrodynamic shear (Torkzaban and Bradford, 2016). Such conditions may occur in surfaces with larger roughness fractions or nanoscale charge heterogeneity on smooth surfaces (Bradford et al., 2018), and/or at concave locations (Shen et al., 2018).

4. Conclusions

Natural porous media commonly exhibit pronounced surface roughness. Experimental results, fitted model parameters, and interaction energy calculations demonstrated that nanoscale roughness on the collector surface controlled AgNP retention and release and that these effects were dependent on the solution chemistry. In particular, limited amounts of AgNPs retention occurred in shallow primary minima (e.g., the tops of small roughness asperities) on the relatively smooth sand that was rapidly released when the IS was reduced and the pH increased. Conversely, much more AgNP retention occurred in deeper primary minima (e.g., concave locations between roughness asperities) on the rougher sand that was mainly irreversible to changes in solution chemistry. Collected data from this study provide valuable information and insight on the importance of roughness on the transport and release of AgNPs, the conditions that enhance or reduce the influence of surface roughness, and the correlation of AgNP deposition parameters with surface roughness. This information also indicates that surface roughness properties of porous media can be optimized to enhance or diminish the retention of colloids and nanoparticles for specific engineering or environmental applications.

Acknowledgments

This research was funded by the National Natural Science Foundation of China (Grant NO. 21507015; 51561135012), Guangxi Natural Science Foundation, China (Grant NO. 2015GXNSFCA139015; 2017GXNSFBA198076), and Cultivation Base of Guangxi Key Laboratory for Agro-Environment and Agro-Product Safety (17-259-82). The authors would like to acknowledge the

assistance of Dr. Huijun Yao for SEM measurement.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.113803>.

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